

Heterostructured Fluorohectorite Clay as an Electrochemical Sensor for the Detection of 2,4-Dichlorophenol and the Herbicide 2,4-D

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A mixed-ion, amphiphilic fluorohectorite heterostructure, wherein the galleries are regularly interstratified by hydrophilic inorganic ions (Na^+) and lipophilic onium ions, is shown to be an efficient electrochemical sensor for the specific determination of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) and the pollutant 2,4-dichlorophenol (2,4-DCP) when incorporated at the 5 wt % level into a carbon paste electrode (CPE). The clay-modified electrode was substantially less sensitive to herbicides that lack the aromatic hydroxyl groups needed for oxidation to a quinone (e.g., Illoxan and Furore). Conventional homoionic organoclays with all galleries exclusively occupied by an onium ion surfactant exhibited a lower electrochemical response to 2,4-D and 2,4-DCP oxidation when incorporated into a CPE. Similarly, low current responses were observed for a CPE modified with a homostructured mixed-ion montmorillonite clay with both inorganic ions and organic onium ions co-occupying each clay gallery. The electrochemical response observed for the mixed-ion fluorohectorite heterostructure was attributed to the ability of this unique clay intercalate to achieve electrical neutrality upon oxidation of the dichlorophenoxy moiety through the facile ejection of sodium ions from the segregated inorganic galleries.

Introduction

The monitoring of environmental pollutants is of vital importance for the protection of public health. Biosensors play an important role in environmental monitoring systems, because they are sensitive devices with a broad linear dynamic range. They also have the advantage of being adaptable to microfabrication technology.¹ The fact that functionalized aromatic compounds can be oxidized at solid electrodes has made possible the electrochemical detection of carcinogenic aromatic amines.² The unique properties of carbon paste electrodes (CPEs), which include easy renewal of the electrode surface, low background current, a favorable anodic potential range, and cost-effective preparation,³ have made them especially attractive for the electrochemical detection of environmental pollutants.

Herbicides and their hydrolysis byproducts are the most abundant pollutants found in the environment and in agricultural products.⁴ 2,4-Dichlorophenol (2,4-DCP) and 2,4-dichlorophenoxyacetic acid (2,4-D) are two such

pollutants that have been associated with the occurrence of cancer in humans. Methods for the determination of 2,4-D have included the use of reverse-phase high-performance liquid chromatography with fluorescence detection^{5,6} and the immobilization of monoclonal antibodies on piezoelectric⁴ and gold electrode⁷ sensors. Despite these advances, there is still a need to develop sensor materials that can provide even more robust, efficient, and selective detection of 2,4-D and related pollutants at affordable costs.

Layered silicate clays are recognized for their versatile adsorption and catalytic properties.⁸ Also, their exceptional chemical and thermal stability and their ability to form continuous films have stimulated studies on their use as electrode modifiers^{9–12} and as sensors.¹³ In this paper, we investigate the use of organic onium-

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ion-exchanged forms of smectite clays as modifiers of a carbon paste electrode (CPE) for the electrochemical detection of 2,4-DCP, 2,4-D, and related pollutants containing chlorinated aromatic groups. These so-called organoclays trap organic contaminants through van der Waals interactions with the hydrophobic segments of the onium exchange cations in the gallery regions of the clay.^{14,15} In this way, the organoclay functions as a solid-state partitioning medium for the removal of the pollutant from solution. Thus, a clay-modified CPE can potentially become a unique analytical tool for the detection of a specifically adsorbed redox-active pollutant. One recently discovered organoclay intercalate, namely, an amphiphilic heterostructured fluorohectorite wherein the galleries are regularly interstratified by a hydrophilic inorganic ion (Na^+) and a lipophilic onium ion surfactant,^{16,17} is shown in the present work to be an especially efficient electrochemical sensor for the specific detection of 2,4-D and 2,4-DCP.

Experimental Section

Homoionic Organo Fluorohectorite and Mixed-Ion Fluorohectorite. Homoionic onium-ion-exchanged forms of a synthetic lithium(I) fluorohectorite (Corning, Inc.) were obtained by allowing the clay to react for 24 h with 3.0 mM solutions of $(\text{C}_{16}\text{H}_{33}\text{PBU}_3)\text{Br}$ and $(\text{C}_{16}\text{H}_{33}\text{NMe}_3)\text{Br}$ (where Bu = butyl and Me = methyl) in 2-fold excess of the ion-exchange capacity of the clay. The organo clays were washed free of excess onium ions and air-dried at room temperature.

A synthetic high-charge-density lithium fluorohectorite (Corning, Inc.) was converted to the sodium-ion-exchanged form by reacting it with a 2-fold excess of an aqueous 0.1 M NaCl solution, washing free the excess salt, and allowing the clay to dry in air at ambient temperature. A mixed-ion heterostructure was formed by the reaction of the Na^+ clay and $(\text{C}_{16}\text{H}_{33}\text{PBU}_3)\text{Br}$ at a clay/surfactant molar ratio of 1.0:0.5 in deionized water at room temperature for 48 h. A 3.0 mM aqueous surfactant concentration was used. Excess salt was removed by washing with water before the product was air-dried.

Homoionic Organo Montmorillonite and Mixed-Ion Montmorillonite. A 1% (w/w) suspension of sodium(I) montmorillonite was allowed to react at 50 °C with a 0.5 M aqueous onium ion surfactant solution, $(\text{C}_{16}\text{H}_{33}\text{NMe}_3)\text{Br}$, in 2-fold excess of the clay cation-exchange capacity. After a reaction time of 24 h, the organo montmorillonite product was washed with ethanol and water to remove excess surfactant and air-dried. Nanocor Co. provided the mixed-ion homostructured form of montmorillonites wherein the exchange sites are occupied by 1:1 $\text{Na}^+/\text{C}_{18}\text{H}_{37}\text{NMe}_3^+$.

Physical Measurements. All of the basal spacings of the organo clay products were determined by powder X-ray diffraction. The patterns were obtained on a Rigaku Rotaflex diffractometer equipped with a rotating anode (Cu K_α radiation) operated at 45 kV and 100 mA. The scattering and receiving slits were 1/6° and 0.3°, respectively.

Electrochemical Apparatus. The differential pulse voltammetry (DPV) measurements were done by using an Autolab electrochemical analysis system and GPES 4.8 software package (Eco Chemie, The Netherlands). The three-electrode system consisted of the carbon paste electrode (CPE) as the working electrode, the reference electrode (Ag/AgCl), and a platinum wire as the auxiliary electrode. The body of the CPE was a glass tube (3 mm i.d.) tightly packed with carbon paste.

The electrical contact was provided by a copper wire inserted into the carbon paste. Convective transport, when desired, was provided by a magnetic stirrer.

Electrode Preparation. The modified carbon paste was prepared in two steps. The first step involved a thorough mixing of the desired amounts of graphite powder and mineral oil (Acheson 38, Fisher) [30/70% (w/w) graphite/oil]. An amount of the initial paste was hand-mixed with the desired organoclay to make the clay-modified carbon paste. A portion of the resulting paste was packed into the end of a 3-mm (i. d.) glass tube. Electrical contact was established via a copper wire. The surface was smoothed on a weighing paper. The bare CPE was prepared by following the procedure explained above without the incorporation of clay in the carbon paste matrix.

Procedure. Analyte solutions were prepared from reagent-grade chemicals with deionized water. 2,4-Dichlorophenol (2,4-DCP) was obtained from Sigma. 2,4-Dichlorophenoxyacetic acid (2,4-D), methyl 2-[4-(2,4-dichlorophenoxy)phenoxy]propanoate (Illoxan), and 2-[4-(6-chloro-2-benzoxazolyloxy)phenoxy]propanoate (Furore) were obtained from Hoechst. Stock solutions of 1.0 mM, 2,4-D, Iloxan, and Furore were prepared daily using deionized water, whereas 1.0 mM 2,4-DCP was prepared in tetrahydrofuran and diluted as needed in 0.05 M phosphate buffer (pH 7.40).

Each electrochemical measurement made use of a freshly prepared CPE surface. The experiments were performed at room temperature, 25.0 ± 0.5 °C. All of the buffer solutions contained 20 mM NaCl to establish a constant low ionic strength. The clay-modified CPE was activated by applying +1.70 V for 1 min in a 0.05 M phosphate buffer solution (pH 7.40) without stirring. The activation at +1.70 V is necessary for oxidizing all of the functional groups of the graphite surface to carboxylic forms. This oxidation step is important for the pretreatment and cleaning of the surface from the redox-active interferences. The pretreated clay-modified CPE was then washed with distilled and deionized water for 10 s and transferred into a 50 mM phosphate buffer solution (pH 7.40) containing a certain concentration of the pollutant. The pollutant was subsequently adsorbed onto the clay-modified CPE without the application of a potential for 5 min in the stirred buffer solution with 20 mM NaCl. The electrode was then rinsed with 50 mM phosphate buffer solution (pH 7.40) for 10 s.

The oxidation signals of the pollutants were measured by using DPV in an unstirred 50 mM phosphate buffer solution (pH 7.40) containing 20 mM NaCl. The raw data were treated using the Savitzky and Golay filter (level 2) of GPES software and a moving average baseline correction with a "peak width" of 0.01. Repetitive measurements were carried out by renewing the surface of the CPE and repeating the above assay format.

Results

Figure 1 and Table 1 describe the five organo smectite clays that we used to form the carbon paste electrodes (CPEs). Each clay was modified through the intercalation of an onium ion surfactant so that at least a fraction of the galleries were lipophilic and, therefore, suitable for dispersion in the CPE matrix and the uptake of organic molecules from aqueous solution. The assignment of the gallery structures shown in Figure 1 was made on the basis of the reported basal spacings (see Table 1). Clays 1 and 5 represent *heterostructured* and *homostructured* mixed organic–inorganic ion-exchanged forms of fluorohectorite and montmorillonite, respectively. These two structures differ in the distribution of the organic and inorganic ions in the gallery regions between the silicate layers. Clays 2–4 are *homoionic* onium ion derivatives wherein the surfactant chains adopt lateral bilayer or paraffin-type structures. The significance of each type of gallery structure is provided in the discussion section.

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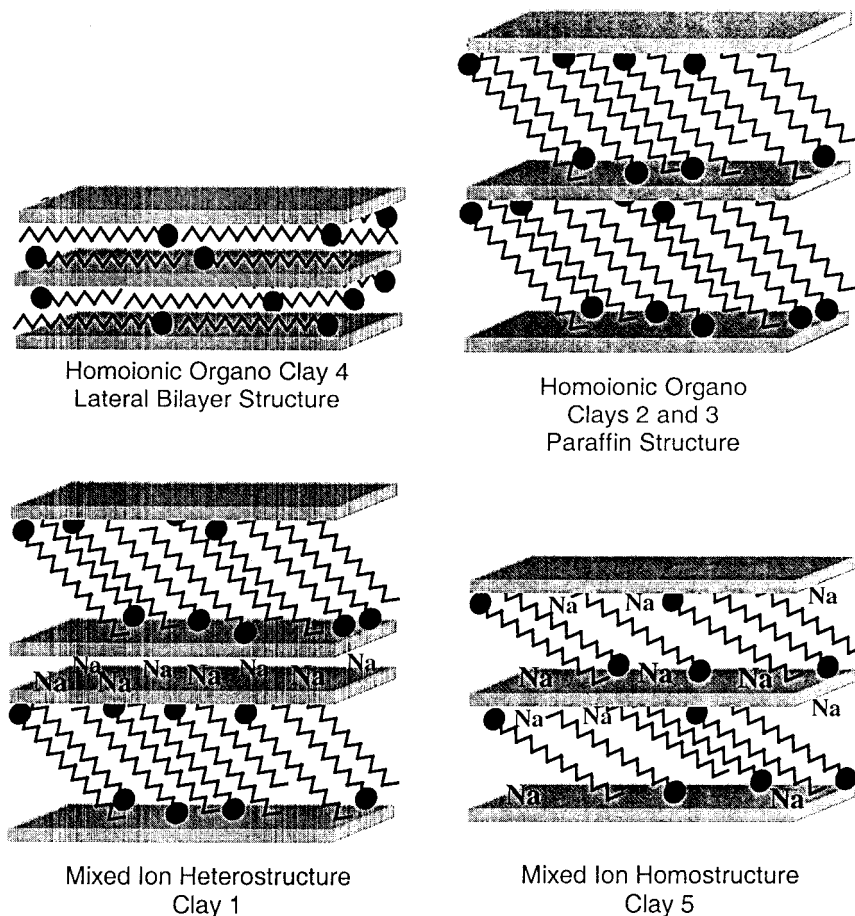


Figure 1. Schematic illustration of the lateral bilayer and paraffin structures of the homoionic organoclays and of the heterostructured and homostructured mixed-ion clays used in this study. For clarity, the alkyl chains of the onium ion surfactant are shown in the all-trans conformation. The basal spacings for each structure type are provided in Table 1.

2,4-Dichlorophenol (2,4-DCP), the herbicide 2,4-D, and the related chlorophenoxy herbicides Illoxan and Furore served as the analytes. The structures of the latter two organics are shown below.

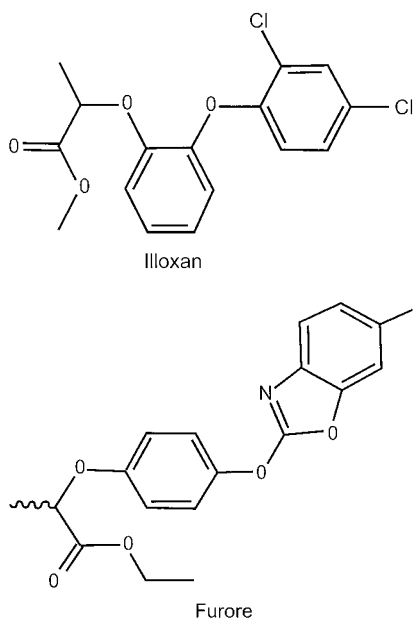


Figure 2 shows the differential pulse voltammograms (DPV) for the oxidative detection of 20 μM 2,4-DCP and 2,4-D after a 5-min accumulation time at a bare CPE

and a CPE modified by the inclusion of 5% (w/w) heterostructured mixed-ion fluorohectorite clay **1**. Part A of the figure shows that the oxidation signal for 2,4-DCP at the clay **1**-modified CPE was substantially larger than the response obtained at the bare CPE. Also, part B of the figure shows that the oxidation signal obtained for 2,4-D was substantially larger for the clay **1**-modified CPE than for the bare electrode.

A series of three independent measurements of the 2,4-DCP and 2,4-D oxidation signals gave reproducible currents with RSD values of 7.20 and 6.73%, respectively. Detection limits of 2.32 and 2.64 $\mu\text{g/L}$ were observed for the voltammetric measurement of 2,4-DCP and 2,4-D, respectively, at a 5% (w/w) clay **1**-modified CPE, as determined by a signal/noise ratio of ~ 3 . This limit of detection for 2,4-D is lower than that recently reported for a piezoelectric immunosensor.⁴ The mean peak currents obtained from 5% (w/w) clay **1**-modified CPE for 2,4-DCP and 2,4-D were 3.42 and 1.22 μA , respectively. In comparison, respective mean peak currents of 0.36 and 0.085 μA were obtained for the bare CPE.

Part C in Figure 2 represents the reduction signals obtained for 20 μM Illoxan after a 5-min accumulation time. The Illoxan response decreased when the CPE was modified with 5% (w/w) clay **1**. The reduction signal for Furore was also lower at the bare CPE than at the 5% (w/w) clay **1**-modified CPE, as illustrated by the curves in part D of Figure 2. It is noteworthy that neither of

Table 1. Gallery Ion Compositions, Basal Spacings, and Gallery Structure Types of the Organoclays Used to Modify Carbon Paste Electrodes

clay sample	clay type	gallery ions (M ⁺)	basal spacing (Å) ^a	gallery structure type
1	fluorohectorite ^b	1:1 Na ⁺ /C ₁₆ H ₃₃ PBu	39	mixed-ion heterostructure
2	fluorohectorite	C ₁₆ H ₃₃ PBu ₃	28	paraffin
3	fluorohectorite	C ₁₆ H ₃₃ NMe	27	paraffin
4	montmorillonite ^c	C ₁₆ H ₃₃ NMe	22	lateral bilayer
5	montmorillonite	1:1 Na ⁺ /C ₁₈ H ₃₇ NMe	22	mixed-ion homostructure

^a Spacings observed for air-dried samples. ^b Unit cell formula: M⁺_{1.12}[Mg_{4.88}Li_{1.12}Si₈O₂₀F₄. ^c Unit cell formula: M⁺_{0.90}[Mg_{0.54}Al_{3.46}](Al_{0.36}Si_{7.64})O₂₀(OH)₄.

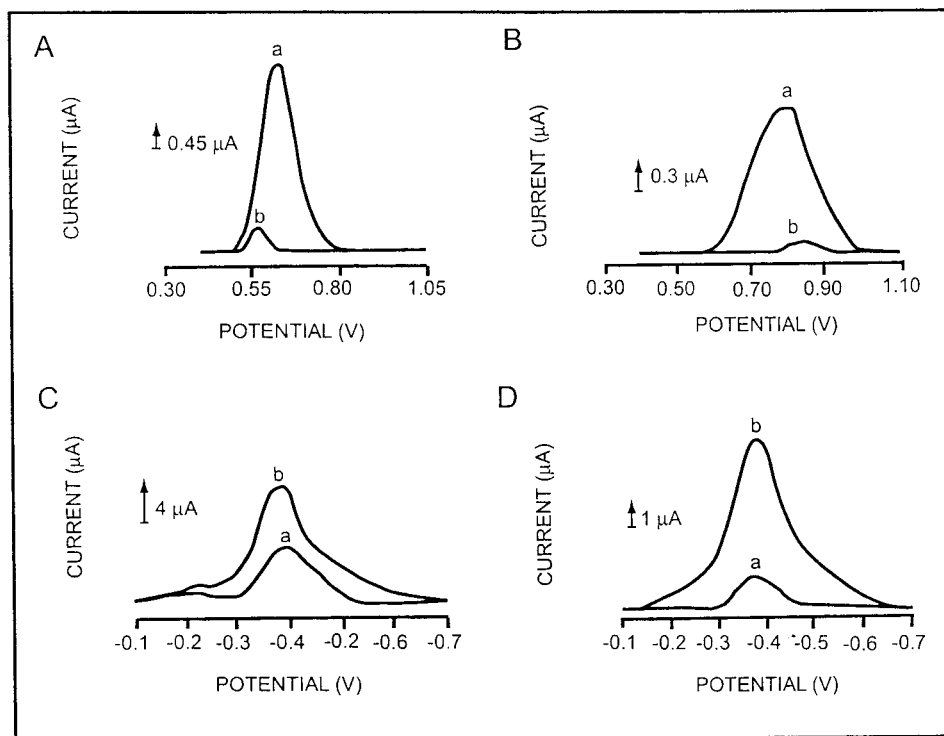


Figure 2. Differential pulse voltammograms (DPV) for 20 μM (A) 2,4-DCP and (B) 2,4-D, (C) Illoxan, and (D) Furore at (a) a 5% (w/w) heterostructured clay 1-modified CPE and (b) a bare CPE. The CPE was pretreated for 1 min at +1.70 V in 0.05 M phosphate buffer (pH 7.40). The pollutant accumulation time was 5 min in stirred 50 mM phosphate buffer solution (pH 7.40) containing 20 μM pollutant. The accumulated pollutant in the blank 50 mM phosphate buffer solution (pH 7.40) containing 20 mM NaCl was determined by DPV (5 mV amplitude).

these analytes showed *oxidation* signal comparable to those observed for 2,4-DCP and 2,4-D, owing to the lack of oxidizable aromatic hydroxyl groups in these structures. The mean peak currents ($\sim 7\%$ RSD values) for the reduction of 20 μM Illoxan and Furore at a 5% (w/w) clay 1 CPE were 6.86 and 1.4 μA , respectively, whereas the respective mean peak currents obtained at a bare CPE were 17.14 and 7.12 μA . The higher reductive currents at the bare electrode indicate that the partitioning of these analytes in redox-active form favors the graphite surfaces over the clay surfaces for these two analytes.

All of the above peak currents were obtained in buffer solutions containing 20 mM NaCl to establish a constant low ionic strength. The ionic strength plays an important role in the diffusion of electroactive species to the electrode surface. A low ionic strength was preferred for the intercalation of the organic planar molecules into the clay interlayers. The dependence of the current response on the ionic strength was also studied (not shown). The current response toward 2,4-D increased linearly to 20 mM NaCl concentration, then started to decrease at higher NaCl concentrations, and reached

an almost constant value between 50 and 100 mM. The decrease of the current signal was attributed to the coverage of the intercalation sites by sodium ions and the exclusion of 2,4-D between the clay interlayers in the presence of excessive ionic strength.

Figure 3 displays the ratios of the electrochemical signals obtained from the clay-modified CPE and bare CPE systems in the presence of each analyte. The oxidative 2,4-DCP and 2,4-D currents obtained with the clay 1-modified CPE are substantially higher than the currents observed with the bare CPE. However, no increase in the 2,4-DCP and 2,4-D signals was observed with the other clay-modified electrodes. In fact, small decreases in current were observed, presumably because of the partial blocking of the electrode surface by the clay and insufficient analyte uptake or electron transfer to the 2,4-DCP and 2,4-D adsorbed at the surfaces of clays 2–5.

The effects of the clay 1 loading on the 2,4-DCP and 2,4-D signals are shown in parts A and B of Figure 4. The 2,4-DCP reached signal saturation at about 7.5% loading of the clay. An increase in clay 1 loading in the carbon paste matrix beyond 7.5% did not increase the

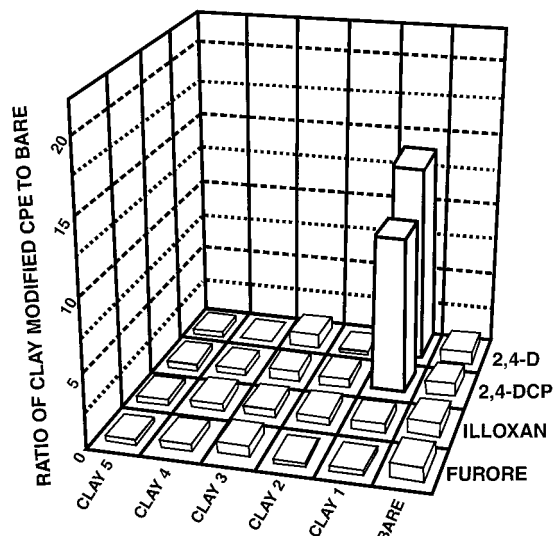


Figure 3. Electrochemical responses observed for various pollutants at 5% (w/w) clay-modified CPE systems, normalized with respect to the response at the bare CPE. The reaction conditions are as described in Figure 2.

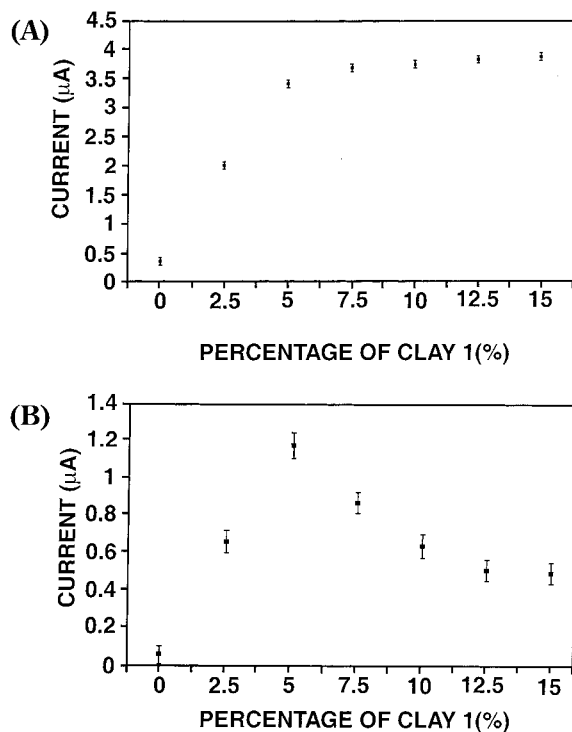


Figure 4. Relationship between heterostructured clay 1 loading in the CPE and the voltammetric signals of (A) 2,4-DCP and (B) 2,4-D. See Figure 2 for reaction conditions.

current signal, indicating the presence of a maximum number of accessible redox sites at the solution–electrode interface. The response provided by the larger 2,4-D analyte reached a maximum signal at an even lower clay loading (~5%), and then the signal response decreased beyond this loading. The presence of an excessive amount of clay 1 in the CPE and its interactions with the analyte can alter the stacking properties of the clay layers and the orientation of the clay particles at the solution–electrode interface, as well as the packing of the clay tactoids between the carbon grains. One or more of these processes could alter the accessibility of the analyte to the electrochemically active

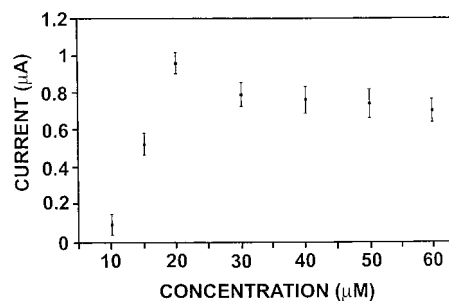


Figure 5. Relationship between current response at a 5% (w/w) clay 1-modified CPE and the concentration of 2,4-DCP. See Figure 2 for reaction conditions.

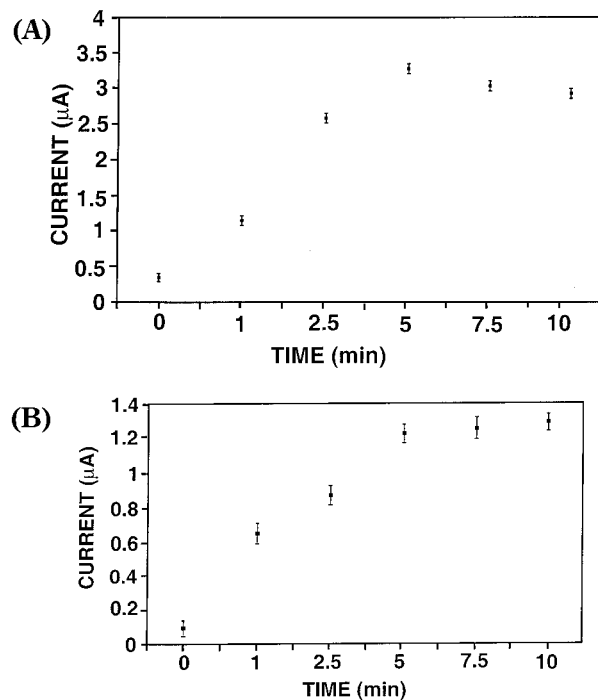


Figure 6. Effect of accumulation time on the voltammetric signals observed for (A) 2,4-DCP and (B) 2,4-D at a CPE modified with 5% (w/w) heterostructured clay 1. The reaction conditions are as described in Figure 2.

sites in the electrode. Whatever the reason for the fall off in signal response at higher clay loadings, the optimum percentage of clay for incorporation into the CPE was chosen to be 5% for further experiments.

Figure 5 displays the analyte concentration dependence of the 2,4-DCP signal at a 5% (w/w) clay 1-modified CPE. The increase with analyte concentration was found to be linear below 20 μM , as expected for the partitioning of the analyte at the clay surface. However, the current response then decreased with further increase in concentration. This latter behavior suggests that excessive binding of the analyte to the clay blocks electron transport at the electrochemically active sites, perhaps as a result of competitive adsorption at inactive sites (e.g., edge sites) that limit access to the redox-active basal plane sites. For subsequent experiments, the analyte concentration was chosen as 20 μM .

Parts A and B of Figure 6 show the effect of analyte accumulation time on the 2,4-DCP and 2,4-D oxidation signals at a 5% (w/w) clay-1 modified CPE. The signals for both 2,4-DCP and 2,4-D rapidly increased up to 5-min accumulation time and then reached a plateau

as the binding to the adsorption sites approached equilibrium. Consequently, 5 min was chosen as the analyte accumulation time for all experiments.

The detection of mixtures containing 20 μM concentrations of 2,4-DCP and 2,4-D in 50 mM phosphate buffer solution (pH 7.40) also was possible using the clay 1-modified CPE. The uptake of the smaller planar structure of the 2,4-DCP molecule apparently was favored, as indicated by the higher current signal for 2,4-DCP in comparison to 2,4-D. Thus, the presence of both 2,4-DCP and 2,4-D in a mixture can be observed at a clay 1-modified CPE, but the current responses are not directly proportional to the relative concentrations of the analytes because of differences in analyte uptake.

Discussion

As shown schematically in Figure 1, all of the organoclays used in this study contained hydrophobic onium ion surfaces for the adsorption of organic molecules from aqueous solution. Unlike the purely inorganic ion-exchange forms of the same clays, which are immiscible in a mineral oil medium, each organoclay could be dispersed readily in a CPE matrix. Nevertheless, only one organoclay derivative, namely, heterostructured fluorohectorite clay 1, was especially effective in providing an improved electrochemical response to 2,4-DCP and 2,4-D when incorporated into a CPE. To better understand the unique performance properties of this clay, we considered the structures of the five clays under investigation.

The orientation of an onium ion surfactant on the gallery surfaces of a smectite clay is determined by the volume of the hydrophobic segment of the ion and the anionic charge density on the silicate layers.¹⁸ For onium ions with alkyl chain lengths of ~ 8 –20 carbon atoms and charge densities corresponding to 0.4–0.9 electron charge units per $\text{O}_{20}(\text{OH},\text{F})_4$ unit cell, the gallery onium ions adopt a lateral monolayer, bilayer, or pseudo-trilayer orientation, wherein the alkyl chains are oriented more or less parallel to the gallery surfaces. Homoionic clays 2–4 in Figure 1 and Table 1 are intercalated by surfactant onium ions with lateral bilayer and paraffin orientations in the galleries. For clarity, the alkyl chains of the surfactant are represented in an all-trans configuration, but in actuality, the chains are almost certainly kinked and intertwined, as indicated by previously reported vibrational spectroscopy¹⁹ and modeling experiments.²⁰ The lateral bilayer intercalate is distinguishable on the basis of a basal spacings of about 18 Å when the galleries are anhydrous. The co-intercalation of water in the gallery region can increase the basal spacings by 2–4 Å. Thus, the basal spacing of ~ 22 Å for air-dried (hydrated) homoionic $\text{C}_{16}\text{H}_{33}\text{NMe}_3^+$ -montmorillonite (clay 4) is consistent with a lateral bilayer structure or, alternatively, a pseudo-trilayer structure.

Increasing the clay layer charge beyond 1.0 electron charge units per $\text{O}_{20}(\text{OH},\text{F})_4$ unit cell, as in fluorohectorite, can result in onium ion orientations that can be either a lateral pseudo-trilayer structure (basal spacing

under dry conditions ~ 23 Å) or a paraffin structure (basal spacing > 23 Å). For $\text{C}_{16}\text{H}_{33}\text{NMe}_3^+$ -fluorohectorite (clay 3) and $\text{C}_{16}\text{H}_{33}\text{PBu}_3^+$ -fluorohectorite (clay 2), the observed spacings are 27–28 Å, consistent with a paraffin orientation of onium ions (see Figure 1).

The mixed organic/inorganic ion derivatives represented by clays 1 and 5 in Figure 1 and Table 1 have both Na^+ ions and onium ions occupying the gallery exchange sites in a 1:1 molar ratio. However, as indicated by the basal spacings (cf. Table 1), these two clays adopt very different gallery structures. For the mixed-ion montmorillonite intercalate (clay 5), the basal spacing is ~ 22 Å, as expected for a mixed-ion homostucture wherein the inorganic Na^+ and organic $\text{C}_{18}\text{H}_{37}\text{NMe}_3^+$ ions co-occupy each gallery region in a stacked array of silicate layers (cf. Figure 1). In contrast, the 39-Å basal spacing of clay 1 is indicative of a heterostructured distribution of exchange cations wherein the hydrophilic inorganic ions (Na^+) and hydrophobic $\text{C}_{16}\text{H}_{33}\text{PBu}_3^+$ onium ions are segregated into regularly alternating galleries. It has been previously shown that heterostructured mixed-ion fluorohectorites are amphiphilic.^{16,17} The inorganic galleries readily adsorb polar molecules (e.g., water), whereas nonpolar species readily adsorb into the organic galleries.

The faradaic current observed at a clay-modified CPE will depend in part on the amount of redox-active analyte at the electrode surface and the partitioning of the analyte between the mineral oil, carbon, and clay phases comprising the electrode. Previous studies of the electrochemical activity of clay-modified electrode surfaces have shown that the electrochemical response provided by a gallery-intercalated guest depends critically on the ability of the clay phase to achieve electrical neutrality upon electron transfer between the electrode and redox-active guest.¹¹ Changes in the valence of lattice Fe^{II} and Fe^{III} impurities in the silicate layers provide one plausible mechanism for achieving charge neutrality.²¹ The other general mechanism involves the shuttling of electrolyte into or out of the gallery region of the clay.¹¹ However, neither mechanism is generally efficient, particularly when organic ions occupy the ion-exchange sites on the basal surfaces. Consequently, the observed current densities are generally low even at high loadings of redox-active gallery guest. With the exception of the CPE modified by heterostructured clay 1, the current responses observed in the present work for the oxidation of 2,4-DCP and 2,4-D are even lower for the clay-modified CPE than for the bare CPE. Presumably, clay phases 2–5 also allow analyte access to the electrode surfaces by adsorbing to the hydrophobic onium ion surfaces, but only the mixed-ion fluorohectorite heterostructure (clay 1) improves the current response to 2,4-DCP and 2,4-D when incorporated into the CPE.

We attribute the enhanced current densities in the case of heterostructured clay 1 to the presence of comparatively high concentrations of 2,4-DCP and 2,4-D on the clay mineral surfaces and to the ability of the heterostructure to achieve electrical neutrality upon analyte oxidation by rapidly desorbing sodium ions from the segregated inorganic galleries. This mechanism for

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achieving electrical neutrality might also explain why the oxidative response of 2,4-DCP was found to decrease with increasing analyte concentration above 20 μM (cf. Figure 5). Excessive binding of the analyte at the clay edges might limit the release of sodium ions from the inorganic galleries, thereby reducing the ability of the clay to achieve electrical neutrality upon electron transport. Although homostructured clay **5** also contains sodium ions (see Figure 1), these ions are apparently less mobile when coadsorbed in hydrophobic galleries along with surfactant onium ions. Consequently, the electrochemical activity of homostructured clay **5** is unremarkable in comparison to that of heterostructured clay **1**.

The decrease in current density that occurs at clay **1**-modified CPEs at loadings above 5% (cf. Figure 4) most likely arises from a change in the packing of the clay tactoids at the CPE–solution interface. Regardless of the clay loading, the clay-modified CPE containing heterostructured clay **1** is far more responsive toward 2,4-DCP and 2,4-D oxidation than it is toward Illoxan and Furore. Although these latter herbicides also contain chlorinated aromatic rings and undoubtedly adsorb onto the surfaces of heterostructured clay **1**, they lack the redox-active hydroxyl groups needed for oxidation to a quinone. In addition, these particular analytes are large in comparison to 2,4-DCP and 2,4-D, suggesting that the partitioning of the analyte between the surfactant galleries of the heterostructure and the carbon grains of the CPE might be different for the heavier pollutants because of steric inhibition of the adsorption process. The somewhat higher reductive current densities provided by Illoxan and Furore at the bare CPE

(see Figure 2) might indicate that the adsorption of these heavier analytes is favored over that of 2,4-DCP and 2,4-D at the carbon grains of the CPE.

Conclusions

In this study, a highly sensitive clay-modified CPE was evaluated using the specific interactions of a heterostructured fluorohectorite clay **1** (see Figure 1) with 2,4-D and 2,4-DCP. The environmentally important pollutant 2,4-DCP and the widely applied herbicide 2,4-D can be readily detected at low concentrations using a carbon paste electrode that has been modified through the incorporation of this amphiphilic clay at the 5 wt % level. The high sensitivity, speed, simplicity, and extremely low cost make the clay-modified CPE an attractive alternative to other analytical methods used for industrial, clinical, and environmental applications. The clay-modified CPE provides a basis for a remote sensor that can be produced by microfabrication technology and used in field detection systems analogous to those developed for the determination of organophosphate pesticides.²²

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